

CLAIMS

1. A batchwise process for the manufacture of an optical fiber made of polymers, this fiber comprising a core and a sheath, the core being formed from a first polymer based on methyl methacrylate and optionally on a (meth)acrylic ester other than methyl methacrylate and the sheath being formed from a second polymer having a lower refractive index than that of the core, this process being characterized in that the process is carried out in an in-line plant ranging from a device for the purification of the starting materials to a spinning device, involving the intermediacy of the various devices of the in-line plant and the various transfer means connecting the various devices of the in-line plant, this plant being leaktight to the external air and to dust and sheltered from light, in particular ultraviolet radiation, and in that the process comprises the following stages:

(1) beads of the first polymer are prepared by suspension polymerization of purified methyl methacrylate and optionally of at least one purified (meth)acrylic ester other than methyl methacrylate in demineralized, filtered and deoxygenated water, the polymerization being carried out in the presence of at least one radical polymerization initiating agent, of at least one chain-transfer agent and of at least one suspending agent and in the virtually complete absence of polymerization inhibitor and of impurities, such as:

(a) biacetyl, in an amount reduced to at most 1 ppm with respect to the total amount of monomers,

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- (b) transition metal ions capable of giving strong light absorption in the visible region,
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- (c) dust and particles, the various abovementioned starting materials used in the suspension polymerization having been filtered before polymerization with
- 10 a filtration threshold of 0.1 micron;
- the polymerization also being carried out with stirring, under an atmosphere of an inert gas;
- 15 (2) on conclusion of stage (1), the beads are separated and washed using demineralized and dedusted water and are dried under an atmosphere of a dedusted and preferably inert gas, and the dried
- 20 beads are stored under this atmosphere in at least one intermediate tank;
- (3) at least a portion of the beads obtained on conclusion of stage (2) is
- 25 transferred, still under an atmosphere of an inert and dedusted gas, from the intermediate tank or tanks to a coextrusion device and the core of the fiber, starting from said beads, and the
- 30 sheath of the fiber, starting from a polymer having a lower refractive index than that of the core, are coextruded;
- (4) the fiber obtained at the outlet of the
- 35 coextrusion device is gradually cooled, so as to avoid quenching the first polymer intended to constitute the core of the fiber, and the fiber is drawn, in order to obtain a fiber with a mean

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total diameter which can vary from 250
to 2 000 microns.

2. The process as claimed in claim 1, characterized
5 in that the first polymer used to form the core of
the optical fiber is obtained by aqueous
suspension polymerization of at least 70 mol% of
methyl methacrylate, this percentage being with
respect to the total number of moles of vinyl
10 monomers.
3. The process as claimed in claim 2, characterized
in that the first polymer used to form the core of
the optical fiber is obtained by aqueous
15 suspension polymerization of at least 90 mol% of
methyl methacrylate, this percentage being with
respect to the total number of moles of vinyl
monomers.
- 20 4. The process as claimed in claim 1, 2 or 3,
characterized in that the (meth)acrylic ester
other than methyl methacrylate used to prepare the
first polymer used to form the core of the optical
fiber is chosen from the group consisting of ethyl
25 acrylate, ethyl methacrylate, methyl acrylate,
propyl acrylate, propyl methacrylate, butyl
acrylate and butyl methacrylate.
5. The process as claimed in any one of the preceding
30 claims, characterized in that the methyl
methacrylate and the methacrylic ester or esters
used to prepare the beads of the first polymer by
aqueous suspension polymerization are purified by
subjecting them separately to:
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 - an operation of filtration through a bed of
basic and activated alumina, preferably under
an atmosphere of an inert and dedusted gas, in
order to at least partially remove the

compounds possessing labile hydrogen, the highly polar compounds, such as biacetyl, and the polymerization inhibitor;

- 5 - followed by at least two successive operations
of distillation under partial vacuum and under
an atmosphere of an inert and dedusted gas, so
that, on conclusion of these distillation
operations, virtually all the polymerization
10 inhibitor, the biacetyl and the transition
metal ions have been removed;
- and, finally, an operation of filtration under
an atmosphere of an inert and dedusted gas,
15 making it possible to remove virtually all the
particles or dust with a mean diameter of
greater than or equal to 0.1 μm ;

and in that the purified methyl methacrylate and
20 the purified (meth)acrylic ester or esters are
subsequently conveyed directly to the
polymerization reactor via hermetically closed
means while maintaining them under an atmosphere
of an inert and dedusted gas.

6. The process as claimed in claim 1, characterized in that the polymerization initiating agent is purified either by distillation or by recrystallization, the operation being carried out under an atmosphere of an inert and dedusted gas, and in that the purified polymerization initiating agent is transferred into the polymerization reactor via means leaktight to the external air and to dust while maintaining this agent under an atmosphere of an inert and dedusted gas.
7. The process as claimed in claim 1, characterized in that the chain-transfer agent is purified by distillation with the operation being carried out

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under an atmosphere of an inert and dedusted gas,
and in that the distilled chain-transfer agent is
transferred into the polymerization reactor via
means leaktight to the external air and to dust
while maintaining this agent under an atmosphere
of an inert and dedusted gas.

8. The process as claimed in claim 1, characterized
in that the suspending agent is purified by
recrystallization, the operation being carried out
under an atmosphere of an inert and dedusted gas,
and in that the recrystallized suspending agent is
transferred into the polymerization reactor via
means leaktight to the external air and to dust
while maintaining this agent under an atmosphere
of an inert and dedusted gas.

9. The process as claimed in any one of the preceding
claims, characterized in that the suspension
polymerization reaction is carried out under a
pressure substantially equal to atmospheric
pressure or slightly greater.

10. The process as claimed in any one of the preceding
claims, characterized in that, among the dried
beads of the first polymer which are obtained from
the conclusion of stage (2), those with a mean
diameter of less than 200 microns are removed.

11. The process as claimed in claim 10, characterized
in that, to prepare the core of the optical fiber,
only the dried beads of the first polymer with a
mean diameter varying from 500 microns to 2 mm are
retained.

12. The process as claimed in any one of the preceding
claims, characterized in that the suspension
polymerization is carried out in order to prepare
a first polymer, in the form of beads, the weight-

average molecular mass ($\overline{M_w}$) of which varies from 100 000 to 200 000 with a polydispersity (P) of the order of 2.

- 5 13. The process as claimed in any one of the preceding claims, characterized in that the level of unreacted residual monomers on conclusion of the suspension polymerization reaction is less than 2 mol% with respect to the total of monomers used
10 in the implementation of this polymerization.
14. The process as claimed in any one of the preceding claims, characterized in that the operations of separation, washing, drying, storing and transfer
15 of the beads of the first polymer used to prepare the core of the optical fiber are carried out under an atmosphere of an inert and dedusted gas.
15. The process as claimed in any one of the preceding claims, characterized in that the beads of the first polymer used to prepare the core of the optical fiber are extruded at a maximum
20 temperature of 280°C.
- 25 16. An in-line plant for the implementation of the process as claimed in claim 1, characterized in that it is entirely leaktight to the external air and to dust and sheltered from light and in that it comprises:
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 - means for purifying the methyl methacrylate and, if appropriate, means for purifying at least one (meth)acrylic ester other than methyl methacrylate, these purification means having
35 to make it possible to virtually completely remove the polymerization inhibitor and impurities, such as:

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- means for drying the beads;
 - optionally means for carrying out an antistatic electricity treatment of the beads;
 - 5 - means for storing the beads;
 - means for transferring the beads from the polymerization reactor, involving the intermediacy of the drying means, to the coextrusion plant;
 - 10 - a coextrusion plant comprising at least two extruders:
 - 15 · one or two screw extruders with a degassing region for the formation of the core of the optical fiber;
 - 20 · and a second screw extruder for melting and kneading the second polymer used to form the sheath of the optical fiber;
 - 25 and a device for spinning a composite of the core-in-sheath type;
 - means making it possible to cool, in a gradual and controlled fashion, the optical fiber exiting from the coextrusion plant;
 - 30 - means for drawing the optical fiber in order to achieve a total mean fiber diameter ranging from 250 to 2 000 microns.
- 35 17. The in-line plant as claimed in claim 16, characterized in that the means for purifying the methyl methacrylate and, if appropriate, at least one (meth)acrylic ester other than methyl methacrylate successively comprise:

- 5 - a filter composed of a bed of basic and activated alumina, preferably under an atmosphere of an inert and dedusted gas, in order to at least partially remove the compounds possessing labile hydrogen, the highly polar compounds, such as biacetyl, and the polymerization inhibitor;
- 10 - at least one device for distillation under partial vacuum and under an atmosphere of an inert and dedusted gas, in order to remove virtually all the polymerization inhibitor, the biacetyl and the transition metal ions;
- 15 - and a filter which makes it possible to remove virtually all the particles or dust with a mean diameter of greater than or equal to 0.1 μm .